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SURVEY OF COMMERCIALY AVAILABLE CHEMICAL COATINGS.(U)

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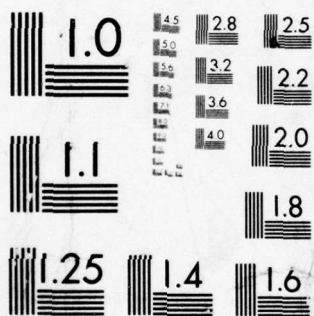
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ED-CR-76038

SURVEY OF COMMERCIALY
AVAILABLE CHEMICAL COATINGS
FINAL REPORT

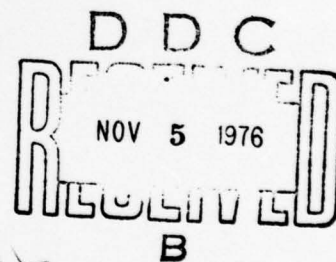
by

M. Luttinger, J. M. Spangler,
D. L. Hill, and J. A. Wray

April 1976

BATTELLE
Columbus Laboratories
Columbus, Ohio 43201

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DEPARTMENT OF THE ARMY
Headquarters, Edgewood Arsenal
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Treating the silicone rubber surface of the Edgewood Arsenal face mask with an oxidizing flame improved wetting and adhesion properties of the silicone. Daran X-226, Alfa 1059, and Cyplex 1600 can act as primers on the silicone surface because of their good adhesion. Several potential barrier coatings were evaluated. Kynar Cyplex or Humiseal 1F54 may be used as top coat since each can increase barrier properties.		

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PREFACE

This work was performed under Contract DAAA15-75-C-0176, Edgewood Arsenal, Aberdeen Proving Ground, Maryland, from June 25, 1975, to October 24, 1975.

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SUMMARY

As part of the development of a new Face Mask, Edgewood Arsenal has selected a silicone rubber compound having good clarity, flexibility, and wide temperature capability. The objective of the present project is to screen a variety of coatings which would add high barrier properties to toxic agents and high abrasion resistance, while maintaining the desirable characteristics of the silicone face mask.

Several candidates giving satisfactory protection to the toxic agents have been identified. Of special interest for further development are two coating systems: (1) a polyvinylidene chloride primer and phenoxy resin topcoat, and (2) a UV-curable barrier coating.

A major problem was to overcome the poor wetting characteristics of the silicone rubber to a variety of polymer solutions and especially to aqueous dispersions and to provide good adhesion between the silicone and the coating interface. Treating the silicone surface with an oxidizing flame proved to be very beneficial in improving both wetting and adhesion characteristics of the silicone.

Several coatings were identified which can act as primers on the silicone surface by virtue of their good adhesion. The best candidates in this group of coatings were polyvinylidene chloride (Daran X-226), thermoplastic polyurethane (Alfa 1059), and thermosetting polyester (Cyplex 1600).

Several potential barrier coatings were applied and submitted to Edgewood Arsenal for evaluation. In addition to the Daran and Cyplex coatings, which could perform dual functions, a polyvinylidene chloride solution polymer (Saran 300), polyvinylidene fluoride (Kynar 301F and RC-9107-20), phenoxy resin (Bakelite PKHH), rubber hydrochloride (Pliofilm cement), a UV-curable coating, and an Aclar laminate were evaluated.

A top coat may be desirable, if the barrier film requires protection from the solvating action of the toxic agents. This function may be performed by Kynar, Cyplex or a thermosetting acrylic (Humiseal 1F54). Each of these could individually contribute to barrier properties.

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SURVEY OF COMMERCIALLY AVAILABLE CHEMICAL COATINGS

by

M. Luttinger, J. M. Spangler,
D. L. Hill, and J. A. Wray

I. INTRODUCTION

Edgewood Arsenal is in the process of developing a new protective mask which will have significantly greater visibility and is planned to replace all current Army combat type protective masks and the M9A1 Special Purpose Mask. The mask must be able to withstand wide climatic exposure and will be designed for use in the field, in low-performance aircraft, and on U.S. Naval vessels.

A mask with excellent temperature capability, optical clarity, and flexibility has been developed by Edgewood Arsenal from a silicone rubber compound. Its major deficiencies are poor barrier properties to toxic agents and poor abrasion resistance. This program was concerned with screening of candidate protective coatings to improve barrier and abrasion properties, while maintaining other essential features of the mask including good flexibility, clarity, wide-temperature capability, etc.

II. EXPERIMENTAL PROGRAM

During the laboratory investigation, coatings were generally applied from aqueous dispersions or from solutions of resins in appropriate solvents. Some work was also conducted with powder coating techniques using electrostatic spraying and electrostatic powder gravure. Resin dispersions and solutions were most often applied to the silicone rubber panels by dip-coating, because this technique tended to give most uniform results. However, spraying, brushing, and deposition with wire-wound rods were also investigated at various times.

In order to evaluate a wide range of polymer coatings, application techniques and formulation adjustments were not optimized for each of the systems under investigation. For the same reason, protective additives such as antioxidants and UV stabilizers were not incorporated during this preliminary screening phase. Consequently, coating appearance, while believed to be adequate for barrier testing, may be subject to considerable improvement during any followup work.

In consideration of the complex demands placed on the coating of a protective face mask, it was believed to be unlikely that a single polymer could adequately fulfill all the requirements. Most of the panels submitted for testing, therefore, had multiple coatings applied. Occasionally, panels were also submitted with only one or two components of a total coating system, in order to isolate the effect of the toxic agents on specific layers. It is expected that these data will be helpful in the selection of a coating system for final development.

A. Surface Treatments and Primers

1. Thermoplastic Polyesters

Work was initiated with Goodyear's Vitel PE-100, PE-200, and PE-207 linear, saturated polyester resins. Untreated panels were dip-coated with PE-200 in MEK, but the dried films had poor adhesion and marginal flexibility. Mixtures of PE-200/PE-207 in 90/10, 80/20, 70/30, and 60/40 ratios were similarly coated. Adequate flexibility (90-degree bend over 2-inch mandrel) was only obtained with the 60/40 composition. Films of the 70/30 and 60/40 mixtures passed the adhesion test (with 1- by 3-inch Scotch Tape), but only the 60/40 composition passed the Scotch Tape test after cross hatching (cutting an "X" into the film with a razor blade).

From information made available by the manufacturer, it is known that an increase in the ratio of PE-207 in a film tends to detract from the solvent resistance. On the other hand, PE-100 provides maximum solvent and

abrasion resistance, but minimum flexibility within this line of resins. Vitel PE-100 was therefore left for possible evaluation as a topcoat, while alternative solutions to the adhesion problem were sought.

Although completely saturated and of low hydroxyl number, cross-linking of Vitel resins with isocyanates is feasible according to the manufacturer. Such films are reported to have improved hardness and adhesion, and improved solvent and heat resistance, but at a slight sacrifice in flexibility.

For cross linking, Mondur CB-75, a toluene diisocyanate-based adduct from Mobay was employed at 5- and 7.5-percent level based on polyester. PE-200 was dissolved in these experiments in 2-nitropropane to minimize water content of the solvent. In later experiments, 1,2-dichloroethane was substituted because of better performance of the solutions in dip coating.

Coatings were applied over untreated silicone rubber panels and after air drying overnight were cured 20 minutes at 120 C. Adhesion was considerably improved, but flexibility was marginal. Samples of the following coatings were submitted to Edgewood Arsenal for testing:

<u>Formulation</u>	<u>Weight Percent</u>	
	<u>No. 17-1</u>	<u>No. 26-1</u>
Vitel PE-200	19.8	16.5
2-Nitropropane	79.2	-
1,2-Dichloroethane	-	82.7
Mondur CB-75	<u>1.0</u>	<u>0.8</u>
	100.0	100.0

2. Polyvinylidene Chloride

Polyvinylidene chloride polymer is among the outstanding plastics in providing barrier films for conventional applications. It is also frequently used as a tie coating in the lamination of dissimilar films.

The application of coatings on untreated silicone rubber panels was attempted with Daran X-226 and Daran X-801, two latexes from W. R. Grace & Co. Neither of these wetted the silicone surface. Since the X-226 polymer

has reportedly the better barrier properties, it was used exclusively in all future trials.

It was found that panels kept for several days in distilled water at ambient temperature were considerably more wettable with Daran X-226, although occasional bare spots remained. The substitution of dilute acetic acid did not accelerate or improve on this effect. Daran X-226 films dip-coated over prewetted panels and dried 2 hours at 50 C had relatively poor adhesion.

The most successful treatment by far was obtained by exposing the silicone rubber surface to an oxidizing flame. Daran X-226 wetted the flame-treated panels very well and after drying had good adhesion. It was subsequently found that many other polymers also exhibited greatly improved adhesion on flame-treated silicone rubber.

Undiluted Daran X-226 has 60 to 62 percent solids and desposits a relatively thick film on dipping. These films frequently produce surface cracks or "mud cracks" on drying. This is especially prevalent when two films are deposited, which is beneficial in eliminating pinholes for maximum barrier properties.

Attempts to overcoat Daran X-226 diluted with water to about 15 percent solids over Vitel PE-200 ran into difficulties because of poor wetting. Several wetting agents were, therefore, investigated at the 0.5 percent level based on diluted latex, including Silicone L-5310, Aerosol OT, Triton X-100, and Tamol 731 (25%). Higher levels of Tamol 731 were also investigated because of its low solids content. Triton X-100 gave the best results and the following samples were prepared and shipped to Edgewood Arsenal for testing:

Panels 21-1

First coat of Vitel PE-200 including Mondur CB-75 (see 17-1 above)

Second and third coat of Daran X-226 as follows:

	<u>Weight Percent</u>
Daran X-226	33.1
Deionized Water	66.4
Triton X-100	0.5
	<u>100.0</u>

Each Daran coating was separately cured immediately after dipping at 120 C for 1 minute.

3. Other Primers

Alfa 1059 is an aliphatic polyurethane elastomer of good clarity from NL Industries which reportedly has excellent adhesion to many difficult-to-bond surfaces. It also has a wide range of solvent resistance, which is important when overcoating with other polymer solutions. Several grades of this lacquer are available. The one used in this program, Alfa 1059, is 25 percent nonvolatile in 5/1 methyl cellosolve/toluene.

Untreated panels were readily wetted by the Alfa 1059 lacquer and clear, uniform films were deposited. One of these was allowed to air dry for several days, while others were cured at 70 C for 30 minutes and at 104 C for 30 minutes, respectively. All of the films had excellent flexibility, but poor adhesion (Scotch Tape test without cross-hatching).

Another set of Alfa 1059 coatings were applied, this time on flame-treated panels. The coatings were allowed to dry or cure as follows: (a) air dry, (b) air dry 10 minutes and cure at 70 C for 30 minutes, (c) air dry 30 minutes and cure at 177 C for 30 minutes. Those cured under condition (c) were slightly yellow; the others were clear and colorless. All of the panels passed the flexibility and adhesion test (without cross-hatching).

Elvamide 8061 is a polyamide terpolymer from Du Pont which has limited solubility in a few select solvent combinations, unlike other nylon-type polymers which are for practical purposes insoluble. In preliminary powder coating trials (see discussion below), this polymer exhibited good adhesion to silicone panels without flame treatment.

A 12 percent solution of Elvamide 8061 in 1/1 methyl alcohol/trichloroethylene was applied over untreated and flame-treated silicone rubber panels. Some of the coatings were allowed to air dry for 2 hours and some were cured at 177 C for 10 minutes. While good wetting was obtained on both the untreated and flame-treated surfaces with the polymer

solution, only air drying produced continuous films; the oven drying step caused the wet film to shrink away from the surface and produced a discontinuous coating (this was most notable on the untreated panel, and to a lesser extent also on the flame-treated panel). Adhesion was poor on the untreated surfaces, but very good on the flame-treated surfaces (Scotch Tape over cross-hatching).

An 80/20 ratio of Elvamide 8061 and Epon 828 in the same solvents as above was also investigated. This resin combination can be cross-linked at elevated temperature. However, some haziness was observed in these coatings, which could diminish the usefulness of these coatings for the present application.

Coatings of the above resin combination were applied over untreated and flame-treated silicone rubber panels. One set of each was cured for 10 minutes and the other set for 30 minutes at 177 C. Wetting was poor or marginal over the untreated surfaces and adhesion was poor. However, coatings applied over the flame-treated panels exhibited good wetting, good flexibility, and excellent adhesion (Scotch Tape over cross-hatching).

A thermosetting polyester based on Cyplex 1600 was originally designed as a topcoat to protect barrier coatings that may be solvent sensitive. In several instances it was used in this capacity and submitted for testing. However, because of its excellent adhesion to flame-treated panels and very high solvent resistance, it could also serve as a primer.

Flame-treated silicone rubber panels were double-coated by dipping in the solution shown below. Each layer was separately cured at 260 C for 90 seconds;

Panels 28-1

	<u>Weight Percent</u>
Cyplex 1600 (75% solids)	38.0
Cymel 303	7.1
Dimethylaminoethanol	5.3
Catalyst 1010	0.34
Resin XC-4011 (75% solids)	0.74
Silicone Resin L-5310 (10% solids)	1.1
Deionized Water	47.42
	<u>100.0</u>

Cyplex 1600 is a water-reducible, thermosetting polyester (75 percent in 50/50 n-butanol/ethylene glycol monobutyl ether) which is cross-linked with Cymel 303 (hexamethoxymethylmelamine) in the presence of Catalyst 1010. Dimethylaminoethanol helps to solubilize the resin in the aqueous medium and inhibits cross-linking at lower temperatures. Resins XC-4011 and L-5310 are anticratering additives.

Panels 28-1 were submitted to Edgewood Arsenal for evaluation. The coatings had excellent flexibility and adhesion (Scotch Tape over cross-hatching).

B. Barrier Coatings

Most information on barrier properties of commercial polymers involves gas and water vapor permeability. Factors such as film density and degree of crystallinity are frequently identified as important contributors to high-barrier properties. Based on these characteristics, good barrier films are generally effective for a wide range of gases and vapors. Major exceptions can generally be attributed to the presence of diffusing species which have a high solvating effect on the polymeric films.

Until feedback from the testing program becomes available, a good working hypothesis is to assume that the best barrier films identified for vapors and gases, in general, may also be good candidate barriers for the toxic agents under consideration. Further, it appears likely that cross-linked and plasticizer-free coatings have the best chance of resisting any solvating action of the toxic agents.

Several of the primers described in the previous section are also believed to be good candidates for barrier coatings. Foremost among these is the Daran latex, since polyvinylidene chloride copolymers rank high among barrier films in commercial packaging applications. Polyesters also have good barrier properties to conventional gases and vapors, and both the Vitel thermoplastic polyesters and the Cyplex thermosetting polyester resin may contribute barrier properties. However, somewhat thicker coatings as well as multiple coatings may be useful for barrier applications.

1. Polyvinylidene Chloride

In addition to the Daran coatings, Saran resins applied from solvent systems may be of interest. The material selected for investigation was Saran F-300 which produces films of good clarity. This polymer applied from MEK solution did not have good adhesion to silicone rubber surfaces, even after the latter had been flame-treated. It would, therefore, not be a useful primer. However, it may have an advantage over the Daran latex in that additives such as surfactants are absent from the polymer solutions.

Some difficulties were encountered in selecting the proper primer for Saran which has to be applied from a ketone solution. Alfa 1059 is reportedly resistant to ketones; however, it was sufficiently affected to distort see-through clarity of the composite. Daran, which was not expected to withstand the ketone solvents, was apparently softened, but could be used as a primer, if the conditions for complete solvent release without blistering can be determined. Still another alternative would be the use of a thermoset polyester primer.

2. Plioilm

Plioilm is based on rubber hydrochloride and has been widely used in food packaging because of its barrier properties. It is sold in film form, the various grades representing primarily different plasticizer contents. The N-1 grade has the best overall barrier properties and the lowest plasticizer content (only about 3.75 percent). Although somewhat less effective than polyvinylidene chloride, it enjoys a considerable price advantage at equal thicknesses.

Plioilm could be supplied by the manufacturer in the form of a cement using benzene as the solvent. Although of fairly low solids content, the solution gels quickly on standing and has to be reconstituted with stirring at or above 70 C. Only limited work was done with this polymer because of difficulties encountered in producing a uniform coating. However, it is potentially available for future use if price considerations become important.

3. Polyvinylidene Fluoride

Polyvinylidene fluoride polymer, while generally not as good a barrier as polyvinylidene chloride, tends to have much better chemical and abrasion resistance. However, it requires very strong polar solvents and films are difficult to deposit.

Solutions of Kynar 301F and Kynar RC-9107-20 were prepared in DMF. A portion of each of these solutions was further diluted about 50 percent by weight with MEK. Coatings were attempted with these solutions over unmodified silicone rubber, Daran X-226, and Vitel PE-200, respectively. Air drying followed by baking at 100 C and baking of the wet films at 100 C for 1 hour was tried. Wettability and adhesion were marginal. Where the film lifted off the surface, it became hazy to opaque.

4. Phenoxy Resins

Solution coating resins such as Bakelite PKHH are high molecular weight thermoplastics derived from bisphenol-A and epichlorhydrin. They are not usually considered high-barrier coatings, but were thought to be useful in this investigation because of the undetermined barrier requirements of the toxic agents, and because the resins can be readily cross-linked and modified by a wide variety of other resins and polyfunctional additives.

The limited scope of the present program did not permit a thorough evaluation of all the major resin modifications possible with PKHH. The investigation was limited to an examination of the unmodified film and of diisocyanate or aminoresin cross-linked systems.

A preliminary evaluation of coatings prepared from THF solution was carried out with a variety of cross-linking agents as shown in the table. THF, free of moisture (dried over calcium hydride), was used to prevent interference with the diisocyanate cross-linking agents. Coatings were brushed onto untreated silicone rubber panels and after 2 hours air drying were cured at 177 C for 10 minutes.

TABLE. PRELIMINARY EVALUATION OF MODIFIED PHENOXY RESIN COATINGS

Formulation	Resin (a)	Modifier (b)	Modifier on Resin, percent	Observations (c)
24-1	PKHH	--	--	good adhesion to untreated polysiloxane
24-2	PKHH	Petrarch G-6720	5	good adhesion to untreated polysiloxane
24-3	PKHH	Hylene T	30 (d)	opaque, brittle, good adhesion
24-4	PKHH	Mondur HCB	(e)	slightly hazy, very brittle
24-5	PKHH	Petrarch G-6720 Mondur HCB	5 (e)	slightly hazy, very brittle
24-6	PKHH	Petrarch G-6720 Cymel 245-8	5 25	poor flexibility, adhesion could not be tested
24-7	PKHH	Petrarch G-6720 Uformite F-240	5 25	good adhesion to untreated polysiloxane, marginal flexibility

(a) Union Carbide's phenoxy resin dissolved 20 percent by weight in dried THF.

(b) Petrarch G-6720 = 3-glycidoxypopyltrimethoxysilane (Petrarch Systems)

Hylene T = toluene -2,4-diisocyanate (Du Pont)

Mondur HCB = ketoxime-blocked aromatic/aliphatic polyisocyanate, 40 percent NV (Mobay)

Cymel 245-8 = melamine-formaldehyde resin, 50 percent NV (American Cyanamid)

Uformite F-240 = butylated urea-formaldehyde resin, 60 percent NV (Rohm and Haas).

(c) After air drying for 2 hours and curing 10 minutes at 177 C.

(d) 100 percent stoichiometric.

(e) Equivalent to 100% stoichiometric.

The results show that diisocyanate-cross-linked PKHH coatings were very brittle, at least at the high cross-linking levels employed in these experiments. The opacity observed with the coating containing Hylene T suggests that moisture may have interfered with the reaction, probably during the air-drying step. It is interesting, however, that reasonably good adhesion was obtained between the untreated silicone surface and the unmodified resin.

Although Bakelite PKHH may possibly be applied without a primer, it was felt that optimum results could be achieved by applying the phenoxy solution over a double-coated Daran X-226 primer. Blistering was encountered by baking the Daran coatings first at 177 C for 2-1/2 minutes. However, without the prebake, the PKHH overcoating must be dried very gently in order not to raise blisters.

Daran X-226 primed silicone panels were dip coated with Bakelite PKHH in MEK solution, and after a very gradual drying schedule, several blister-free panels (marked 44-1) were obtained and submitted for evaluation. Another set of four panels with minimal blisters were overcoated with Cyplex 1600 and designated 44-2. The following procedures were used:

Panels 44-1

First and second coat of Daran X-226 over flame-treated silicone panels as shown in 21-1.

Third coat of 22.5 percent Bakelite PKHH in methyl ethyl ketone applied by dipping and dried for 2.5 hours at 37.8 C, for 48 hours at ambient temperature, for 10 minutes at 120 C, and for 10 minutes at 177 C.

Panels 44-2

First, second, and third coat as in 44-1.

Fourth coat dipped in Cyplex 1600 dispersion as shown in Formulation 28-1 and cured at 260 C for 90 seconds.

5. UV-Curable Coating

One of the newest fields in coatings technology that has been commercially accepted in industry is the curing of coatings by ultraviolet radiation. Typically, such formulations contain appropriate unsaturated monomers or prepolymers and a UV-sensitive initiator. The cured coatings are generally highly cross linked and solvent resistant. Clear coatings of this type may be quite useful as topcoats for the new face mask, since they can be formulated to have the required flexibility and toughness.

A proprietary, UV-curable coating which had been specially formulated for high-barrier properties was applied directly to flame-treated silicone rubber samples. The cured coating appeared to pass the adhesion and flexibility test satisfactorily. Adjustments in the formulation can be made to optimize these properties together with toughness and barrier characteristics. The following panels were submitted for evaluation:

Panels 57-1

A 20 percent nonvolatile solution in acetone was applied with a No. 34 wire-wound rod over silicone rubber panels which had been flame treated for 75 seconds. The coating was air dried for 30 minutes and exposed to a UV radiation source (2500-w Hanovia lamp) at 100 feet/minute.

During these preliminary experiments, uneven coating thickness was obtained with the available formulation. Better viscosity control and solvent balance will be desirable in an optimized formulation.

6. Aclar Laminate

Aclar is a chlorotrifluoroethylene copolymer film of excellent clarity available from Allied Chemical Corporation. The polymer is not readily soluble in any of the common solvents and the extruded film has outstanding gas and moisture barrier properties. This film could therefore serve both as the principal barrier and as the topcoat.

Since chlorotrifluoroethylene cannot be applied as a coating from a solvent, it was evaluated in the form of a film laminate. For convenience, a readily available laminate of 1.5-mil Aclar 22A and 2-mil PVC from Continental Can Company was laminated by means of an acrylic adhesive to silicone rubber panels as follows:

Panels 48-1

A coating of Monsanto Company's acrylic multipolymer laminating adhesive was applied with a No. 34 wire-wound rod over flame-treated silicone rubber:

Gelva RA-1600 (30-33 percent solids)	25
Methyl Ethyl Ketone	<u>75</u>
	100

After drying at 50 C for 10 minutes, the commercial film (1.5-mil Aclar 22A, 2-mil polyvinyl chloride) was applied with the vinyl side toward the adhesive, and 100-psi pressure was applied for 2 minutes at ambient temperature.

C. Topcoatings

Several of the films discussed under barrier coatings could also form the topcoating, if further evaluation should indicate that the toxic agents do not appreciably solvate the coatings. Cross-linked phenoxy resin and polyvinylidene fluoride, in particular, are good candidates for topcoatings. Moreover, thermosetting systems of various kinds could be considered for topcoatings.

The scope of this program did not permit the study of all the possible systems. Instead, representative candidates were selected among thermosetting polyesters and thermosetting acrylics.

1. Thermoset Polyesters

The coating system based on Cyplex 1600 was already discussed under the section of primer coatings because it had such good adhesion to flame-treated panels. This system has the additional advantage, being primarily an aqueous dispersion, of not attacking most solvent-sensitive layers over which it is deposited.

Panels were coated with Vitel PE-200 and Mondur CB-75 (see 26-1 above) and overcoated twice with Daran X-226 (see Panels 21-1 above). A single coating of Cyplex 1600 formulation (see 28-1 above) was deposited on top of the Daran and subjected to different curing schedules as follows:

Panels 26-2 and 26-3

First coat of Vitel PE-200 in 1,2-dichloroethane with Mondur CB-75 (see 26-1 above). Air dried overnight and baked at 120 C for 20 minutes.

Second and third coat of 1/2 dilution of Daran X-226/ deionized water containing 0.5 percent Triton X-100. Each coating separately baked immediately after dipping at 120 C for 1 minute.

Fourth coat of Cyplex 1600 as described under Formulation 28-1. Cured immediately after dipping by different schedules as follows:

Panel 26-2

177 C for 20 minutes

Panel 26-3

260 C for 90 seconds

By visual observation it could be seen that the topcoats were well cured by both schedules. However, Panels 26-2 had yellowed considerably (probably the Daran layers), while Panels 26-3 showed no signs of yellowing.

Another set of panels very similar to the above, but without the Vitel primer, were prepared and submitted for testing:

Panels 33-3

First and second coat of 1/2 dilution Daran X-226/de-ionized water containing 0.5 percent Triton X-100. Each coating separately baked immediately after dipping at 120 C for 1 minute.

Third and fourth coat of Cyplex 1600 as described under Formulation 28-1. Each coating separately cured immediately after dipping at 260 C for 90 seconds.

Some yellowing was obtained in Panels 33-3 because of a change in technique that resulted in longer exposure to the oven temperature. However, that can be readily avoided in future preparations. Moreover, the addition of heat stabilizers to the Daran coatings should add an extra margin of safety.

As a result of the overcure, the coatings have only marginal flexibility, but adhesion appears to be excellent.

2. Thermoset Acrylic

Type 1F54 thermoset acrylic coating from Humiseal Division of Columbia Technical Corporation was examined as a topcoating. It produces clear, colorless coatings which reportedly have good chemical and solvent resistance, flexibility, adhesion, and mar resistance. Its continuous use operating range is rated as 160 C and it can withstand thermal shock to about -60 C.

Humiseal's Type 1F-54 coating was successfully applied over Alfa 1059 primer. Films of good clarity, flexibility, and adhesion were obtained. The primer apparently was not affected by the solvents in the overcoat. The following panels were submitted for testing:

Panels 52-1

First coat of Alfa 1059 was applied with a No. 34 wire-wound rod over flame-treated silicone rubber:

Alfa 1059 (25 percent solids)	50.0
Isopropyl alcohol	33.3
Toluene	<u>16.7</u>
	100.0

After 10 minutes' air drying, the coating was oven dried for 30 minutes at 70 C.

Second coat of Humiseal's Type 1F-54 diluted 12 percent with xylene was applied with a No. 34 wire-wound rod and dried for 45 minutes at 120 C.

D. Powder Coating Techniques

The objective of this study was to determine whether electrostatic spraying or electrostatic powder gravure can be applied to the coating of silicone rubber protective masks. The polymers investigated were not selected for their usefulness in service, but to evaluate the application techniques. Consequently, polymers were selected for their low melt viscosity and for their ready availability in powder form.

Electrostatic spraying was carried out at 100 kv with Piccolastic E-125 (low molecular weight polystyrene), Piccolyte S-135 (terpene polymer), and Elvamide 8061 (relatively high molecular weight polyamide terpolymer).

At ambient conditions none of the powders had good adhesion to the panel which may be the result of the insulating effect of the silicone rubber. Good powder adhesion was achieved on hot panels with Piccolastic E-125 and Elvamide 8061. However, both of these polymers exhibited very poor wetting

and flowout. It was interesting to note, however, that Elvamide 8061 had good adhesion to the surface.

Because of the difficulties encountered with the spraying technique, electrostatic powder gravure was tried on the same polymer powders as well as on Piccotex LC (low molecular weight vinyl toluene copolymer) and Emerez 1536 (a relatively low molecular weight polyamide). Transfer was evaluated on untreated silicone rubber and on Daran X-226 primed silicone surfaces.

Transfer to both surfaces was very erratic, but was especially bad on the panels having Daran X-226 coatings. Whenever good transfer was obtained, the flowout of the powder on heating was very poor.

It is obvious that major obstacles are encountered in powder coating silicone rubber masks by electrostatic processes. However, it may be possible to improve on the results by increasing the wettability of the surfaces by flame treatment or the proper selection of primers.

E. Evaluation of Barrier Properties of Coatings

The panels submitted to Edgewood Arsenal for evaluation were tested by the Sponsor in duplicate for penetration by two toxic agents: Mustard (HD) and GB. The goal of the program was to achieve at least 6 hours' protection. The following results are expressed in minutes of exposure time until failure:

<u>Panel</u>	<u>Mustard, min</u>	<u>GB, min</u>
17-1	110	> 450
21-1	170	300
	435	> 450
26-1	110	347
	110	> 450
26-2	110	300
	315	> 450
26-3	110	> 450
	110	> 450

<u>Panel</u>	<u>Mustard, min</u>	<u>GB, min</u>
28-1	110	> 450
	110	> 450
33-3	265	202
	265	322
40-1	117	202
	117	202
44-1	450	337
	450	450
44-2	450	202
	450	337
48-1	450	202
	450	450
52-1	265	450
	282	450
57-1	402	322
	450	450

The objective in this preliminary study was to survey a large variety of potential barrier coatings. Consequently, it was not possible to optimize coating compositions and application conditions, and defects of the protective barrier may have occurred in spots. Based on these considerations, the longer penetration times in a set of duplicate determinations are believed to be more trustworthy.

Several coatings show promise of inhibiting the penetration of the two toxic agents past the 6-hour required period. They include 21-1 (thermo-plastic polyester overcoated with polyvinylidene chloride copolymer), 44-1 (polyvinylidene chloride copolymer overcoated with phenoxy resin), 48-1 (lamination with 2-mil vinyl chloride, 1.5-mil Aclar sheet), and 57-1 (UV-cured barrier coating). In addition, several coatings have good resistance to one of the toxic agents. It should be possible, therefore, to combine coatings that resist each of the toxic agents, respectively, to obtain a coating system that is satisfactory for both.

III. CONCLUSIONS

Several coating combinations evaluated in this preliminary program have been shown to provide good protection against the two toxic agents for at least 6 hours. Probably of greatest interest are polyvinylidene chloride primers overcoated with phenoxy resin and the proprietary UV-curable coating. Polyvinylidene chloride copolymer coating over a thermoplastic polyester also gave good barrier properties, but may require an additional topcoat for abrasion or scuffing resistance. As expected, the Aclar laminate performed very well as a barrier against the toxic agents. However, it is uncertain whether a manufacturing process requiring lamination is feasible and the high cost of Aclar detracts from the usefulness of this system.

A major technical barrier to providing satisfactory coatings for the new protective mask is the high release characteristic associated with silicone polymers. Many potential coatings do not adhere well to the unmodified silicone surface. In the course of the present investigation, it was found that surface treatment of the silicone rubber with an oxidizing flame greatly improves the wetting and the adhesion of many polymer coatings to the silicone surface. Wetting of the silicone by aqueous dispersions is also enhanced by prolonged soaking of the rubber in an aqueous medium. However, adhesion was not generally improved thereby.

Other factors which can improve the adhesive bond between the silicone surface and polymer coatings are reactive bridging constituents such as diisocyanates, reactive resins, and silane coupling agents. Coatings of desirable barrier characteristics which cannot be satisfactorily bonded to the silicone surface can be applied over an appropriate primer which has good adhesion to both the silicone and the polymer. Several such primers have been identified including a polyvinylidene chloride latex, a thermoplastic polyurethane, and a thermosetting polyester.

Barrier properties are being evaluated on panels submitted to Edgewood Arsenal and will be discussed in greater depth as the data become available.

There may be a need for a separate topcoat in those instances where the barrier coating may have insufficient chemical resistance to the toxic agents or environmental conditions or is deficient in abrasion resis-

tance. A wide range of topcoats is feasible, but thermosetting resins are believed to be among the best ones available. Those investigated in this program include a thermosetting polyester and a thermosetting acrylic.

A number of good candidate coatings and coating systems have been identified in this preliminary survey and are ready for final development.

IV. FUTURE WORK

The survey phase of the coatings program has identified several candidates which offer satisfactory resistance to the toxic agents. Guided by the conclusions from these tests, the following steps are envisioned for the development of an optimized coating system:

- (1) Investigate alternative resins and composition variables of the most promising polymers.
- (2) Investigate the use of additives such as antioxidants, heat and UV stabilizers, bonding aids, and curing agents for the preferred polymer system.
- (3) Optimize solvent selection and application conditions for the best coating system.
- (4) Evaluate the physical properties of an optimized system.

The optimization studies will also address questions such as the need for a two- or three-component coating and the benefits of depositing multiple layers of a coating to minimize gas and vapor permeability through defects such as pinholes.

APPENDIX
DATA FOR MATERIALS USED, AND FOR PANELS COATED
LIST OF RAW MATERIALS AND SUPPLIERS

Material	Description	Supplier
Aclar	Chlorotrifluoroethylene copolymer film	Allied Chemical Corporation
Aerosol OT	Anionic surfactant	American Cyanamid Co.
Alfa 1059	Solution of elastomeric aliphatic polyurethane	NL Industries, Inc.
Bakelite PKHH	Phenoxy resin	Union Carbide Corporation
Catalyst 1010	Organic acid catalyst	American Cyanamid Co.
Cymel 245-8	Melamine-formaldehyde resin	American Cyanamid Co.
Cymel 303	Hexamethoxymethylmelamine	American Cyanamid Co.
Cyplex 1600	Reactive, water reducible polyester	American Cyanamid Co.
Daran X-226	Polyvinylidene chloride copolymer emulsion	Dewey and Almey Chem. Div., of W. R. Grace & Co.
Daran X-801	Polyvinylidene chloride copolymer emulsion with waxy component	Dewey and Almey Chem. Div., of W. R. Grace & Co.
Elvamide 8061	Nylon-type polyamide terpolymer	E. I. Du Pont de Nemours & Co.
Emerez 1536	Fatty acid-based polyamide	Emery Industries, Inc.
Epon 828	Liquid, bisphenol-A/epichlorhydrin based epoxy resin	Shell Chemical Corp.
Gelva RA-1600	Acrylic multipolymer laminating adhesive	Monsanto Company
Humiseal 1F54	Thermoset acrylic lacquer	Humiseal Div. of Columbia Technical Corp.
Hylene T	Toluene -2,4-diisocyanate	E. I. Du Pont de Nemours & Co.
Kynar 301F	Polyvinylidene fluoride	Pennwalt Corp.
Kynar RC-9107-20	Polyvinylidene fluoride	Pennwalt Corp.
Mondur CB-75	Toluene diisocyanate-based adduct	Mobay Chemical Corp.
Mondur HCB	Ketoxime-blocked aromatic/aliphatic polyisocyanate	Mobay Chemical Corp.
Petrarch G-6720	3-Glycidoxypropyltrimethoxysilane	Petrarch Systems, Inc.
Piccolastic E-125	Low molecular weight polystyrene-type resin	Hercules, Inc.
Piccolite S-135	Low molecular weight polyterpene resin derived from beta-pinene	Hercules, Inc.
Piccotex LC	Low molecular weight vinyltoluene copolymer	Hercules, Inc.
Pliofilm Cement	Rubber hydrochloride solution in benzene	Goodyear Tire & Rubber Co.
Resin XC-4011	Composition unknown (acrylic?); used as an anti-crater additive	American Cyanamid Co.
Saran F-300	Polyvinylidene chloride copolymer	Dow Chemical Co.
Silicone L-5310	Silicone surfactant	Union Carbide Corp.
Tamol 731	Anionic surfactant	Rohm and Haas Co.
Triton X-100	Nonionic surfactant	Rohm and Haas Co.
Uformite F-240	Butylated urea-formaldehyde resin	Rohm and Haas Co.
Vitel PE-100, -200, -207	Linear, saturated polyesters	Goodyear Tire & Rubber Co.

LIST OF COATED PANELS SUBMITTED TO
EDGEWOOD ARSENAL FOR TESTING

<u>Panels</u>	<u>Weight, percent</u>	
	<u>No. 17-1</u>	<u>No. 26-1</u>
Vitel PE-200	19.8	16.5
2-Nitropropane	79.2	--
1,2-Dichloroethane	--	82.7
Mondur CB-75 (75%)	<u>1.0</u>	<u>0.8</u>
	100.0	100.0

Coatings were applied over untreated silicone rubber panels and after air drying over night were cured 20 minutes at 120 C.

Panels 21-1

First coat, of Vitel PE-200 including Mondur CB-75 (see 17-1 above)

Second and third coat of Daran X-226 as follows:

	<u>Weight, percent</u>
Daran X-226	33.1
Deionized water	66.4
Triton X-100	<u>0.5</u>
	100.0

Each Daran coating was separately cured immediately after dipping at 120 C for 1 minute.

Panels 28-1

	<u>Weight, percent</u>
Cyplex 1600 (75% solids)	38.0
Cymel 303	7.1
Dimethylaminoethanol	5.3
Catalyst 1010	0.34
Resin XC-4011 (75% solids)	0.74
Silicone Resin L-5310 (10% solids)	1.1
Deionized Water	<u>47.42</u>
	100.0

Flame-treated silicone rubber panels were double coated by dipping in the solution shown above. Each layer was separately cured at 260 C for 90 seconds.

Panels 26-2 and 26-3

First coat of Vitel PE-200 in 1,2-dichloroethane with Mondur CB-75 (see 26-1 above). Air dried over night and baked at 120 C for 20 minutes.

Second and third coat of 1/2 dilution of Daran X-226/deionized water containing 0.5% Triton X-100. Each coating separately baked immediately after dipping at 120 C for 1 minute.

Fourth coat of Cyplex 1600 as described under Formulation 28-1. Cured immediately after dipping by different schedules as follows:

Panel 26-2

177 C for 20 minutes

Panel 26-3

260 C for 90 seconds

Panels 33-3

First and second coat of 1/2 dilution Daran X-226/deionized water containing 0.5% Triton X-100. Each coating separately baked immediately after dipping at 120 C for 1 minute.

Third and fourth coat of Cyplex 1600 as described under Formulation 28-1. Each coating separately cured immediately after dipping at 260 C for 90 seconds.

Panels 44-1

First and second coat of Daran X-226 over flame-treated silicone panels as shown in 21-1.

Third coat of 22.5 percent Bakelite PKHH in methyl ethyl ketone applied by dipping and dried for 2.5 hours at 37.8 C for 48 hours at ambient temperature, for 10 minutes at 120 C, and for 10 minutes at 177 C.

Panels 44-2

First, second, and third coat as in 44-1.

Fourth coat dipped in Cyplex 1600 dispersion as shown in Formulation 28-1, and cured at 260 F for 90 seconds.

Panels 48-1

A coating of Monsanto Company's acrylic multipolymer laminating adhesive was applied with a No. 34 wire-wound rod over flame-treated silicone rubber:

Gelva RA-1600 (30 to 33 percent solids)	25
Methyl Ethyl Ketone	<u>75</u>
	100

After drying at 50 C for 10 minutes, the commercial film (1.5-mil Aclar 22A, 2-mil polyvinyl chloride) was applied with the vinyl side toward the adhesive, and 100-psi pressure was applied for 2 minutes at ambient temperature.

Panels 52-1

First coat of Alfa 1059 was applied with a No. 34 wire-wound rod over flame-treated silicone rubber:

Alfa 1059 (25 percent solids)	50.0
Isopropyl Alcohol	33.3
Toluene	<u>16.7</u>
	100.0

After 10 minutes' air drying, the coating was oven dried for 30 minutes at 70 C.

Second coat of Humiseal's Type 1F-54 diluted 12 percent with xylene was applied with a No. 34 wire-wound rod and dried for 45 minutes at 120 C.

Panels 57-1

A 20 percent nonvolatile solution in acetone was applied with a No. 34 wire-wound rod over silicone rubber panels which had been flame treated for 75 seconds. The coating was air dried for 30 minutes and exposed to a UV radiation source (2500-w Hanovia lamp) at 100 feet/minute.

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